



TITLE:

Preparation of Crystalline Polyaldehydes

AUTHOR(S):

Furukawa, Junji; Saegusa, Takeo; Fujii, Hiroyasu

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ABSTRACTS

omer was an indispensable process.

Recently we found that alumina was a more effective catalyst for amorphous polymerization. Acetaldehyde was easily converted to high polymer without freezing of the monomer.

Furthermore, Natta *et al.* and ourselves succeeded respectively in the preparation of the crystalline polymer of aldehydes by organometallic compounds and metal alkoxide. The crystalline polymer is much less soluble in organic solvents than the amorphous one.

The mechanism of the stereoregular polymerization was considered in connection with several synthetic organic reactions which involve metal alkoxides and carbonyl compounds. The coordination complex of aldehyde to the metal alkoxide seems to play an influential role in the stereoregular polymerization.

Polymerization of Alkylene Oxides

Junji FURUKAWA, Takeo SAEGUSA and Teiji TSURUTA

Bulletin of the Japan Petroleum Institute, 3, 39 (1961)

A review of catalysts for the high polymerization of alkylene oxides was given, from which it was deduced that a metal-oxygen bond was an essential element of active species in most cases.

Then, two catalytic systems which were found in our laboratory were discussed. First, the active species of the system of diethylzinc and water was mentioned, and the reaction mechanism was suggested. The second system consists of an organometallic compound and an acidic oxide such as alumina or silica-alumina. These systems induce anionic polymerization of alkylene oxide and it can be assumed that adsorption of monomer on metal of the metal-oxygen bond plays an influential role both in activation of monomer and in controlling the stereoregularity.

Preparation of Crystalline Polyaldehydes

Junji FURUKAWA, Takeo SAEGUSA and Hiroyasu FUJII

Makromolekulare Chemie, 44, 398 (1961)

We found that some organometallic compounds and metal aldehydes including acetaldehyde, propionaldehyde and trichloroacetaldehyde (anhydrous chloral) to give crystalline polyaldehydes. Crystalline polyacetaldehyde was much less soluble in organic solvents than the amorphous one.

Active species of this polymerization was supposed to be metal alkoxides and the mechanism of polymerization was considered in connection with several syn-

ABSTRACTS

thetic organic reactions which involve metal alkoxides and carbonyl compounds. It was assumed that the coordination of aldehyde to the metal alkoxide was essential in propagation reaction which determined the stereospecificity of the polymer produced.

Cyclopropanes. (XI). Solvent Effect in Partial Asymmetric Synthesis

YUZO INOUE, Shuji INAMASU, Minoru OHNO, H. M. WALBORSKY
and Toshio SUGITA

Journal of the American Chemical Society, **83**, 2962 (1961)

Partial asymmetric syntheses were achieved by the base catalyzed Michael type addition of (–)-menthyl chloracetate to ethyl acrylate. It is not surprising since partial asymmetric syntheses have been reported by the present authors in mechanistically similar condensations of the SN_2 -process: *e.g.* the non-catalytic addition of diazo-compounds to α,β -unsaturated menthyl esters and the Darzens reactions of (–)-menthyl chloracetate with carbonyl compounds leading to glycidic acids. However, changing the solvent medium from poor solvating and low dielectric solvents such as toluene, benzene, diethyl ether, *n*-octane, cyclohexane and decalin to strongly solvating and high dielectric solvents such as N,N-dimethylformamide, hexamethylphosphortriamide, dimethylsulfoxide and nitrobenzene, resulted in a complete reversal of sign in the resulting optically active *trans*-cyclopropane-1,2-dicarboxylic acid. The Michael type condensation in non-polar solvents gave laevorotatory acid in 1.8~3.1% optical yields, whilst in polar solvents the enantiomeric dextrorotatory acid was obtained in markedly better optical yields, 10~11%.

New γ -Glutamyl Peptides in Garlic

TOMOJI SUZUKI, Michiyasu SUGI and Toshio KAKIMOTO

Chemical and Pharmaceutical Bulletin, **9**, 77 (1961)

During hydroponic cultivation of garlic (*Allium sativum*) by using $^{35}\text{SO}_4^{2-}$ for tracer studies, considerable amount of ^{35}S -labeled S-allylcysteine sulfoxide (alliin), S-methylcysteine sulfoxide and 3-methyl-1,4-thiazane-5-carboxylic acid 1-oxide (cycloalliin) were observed.

Besides these ^{35}S -containing amino acids, six new γ -glutamyl peptides were separated. Of these peptides, four were identified as γ -glutamyl-phenylalanine, γ -glutamyl-S-methylcysteine, γ -glutamyl-S-methylcysteine sulfoxide and γ -glutamyl-S- β -carboxy- β -methylethylcysteinyglycine (S-(2-carboxypropyl) glutathione).
